

# PATENT SPECIFICATION

**600,317**

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## COMPLETE SPECIFICATION

### Improved Process for the Low Temperature Polymerisation of Olefinic Materials

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America)

I, JOHN CONRAD ARNOLD, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This application relates to olefinic polymers; relates particularly to copolymers of isoolefins with diolefins; and relates especially to means for controlling the plasticity of olefinic polymers to permit of the optimum plasticity for convenient processing and curing to good tensile strength.

It has been found possible to interpolymerize an isoolefin such as isobutylene with a polyolefin such as butadiene, isoprene, piperylene, or dimethylbutadiene at temperatures ranging from  $-40$  to  $-165^{\circ}\text{C}$ . by the application to the olefinic mixture of a Friedel-Crafts catalyst to yield a polymer having molecular weights ranging from about 20000 up to 150,000 or higher; which polymers are reactive with sulfur and various other curing compounds in a reaction which removes from the polymer the property of cold flow and develops in the material a definite elastic limit, a high tensile strength, a good abrasion and flexure resistance and other valuable physical properties.

This material is fabricated in much the same manner in which natural rubber is fabricated, which requires a considerable amount of processing and extruding. The ease with which such processing can be conducted is found, however, to be a function of the plasticity of the material. Material having a Williams plasticity

above 145, or a Mooney viscosity above 60 is so tough as to be extremely difficult to process on the mill or in the extruder, and material having such a plasticity value is undesirable because of the high power demands for processing, the difficulty of making the material "band" on the mill, and the extreme difficulty of getting smooth extrusion products. Material having a Williams plasticity between 100 and 145, or a Mooney viscosity within the range between 35 and 60 is quite easy to process, since it works easily on the mill, bands readily, extrudes smoothly and rapidly and requires a minimum of power for the processing. Material having a Williams plasticity below 100 or a Mooney viscosity below 35, sticks to the mill, and, when cured, usually has a poor tensile strength. It is found that the Williams plasticity and Mooney viscosity are functions both of the average molecular weight, and the molecular weight range of the material; material having an average molecular weight from 20000 below which the material becomes semiliquid, up to 28000, has a Williams plasticity below 100 and a Mooney viscosity below 35, without regard to the molecular weight range. Material having an average molecular weight above 28000, up to 55000, and a moderately narrow molecular weight range has a Williams plasticity range between 100 and 145 or a Mooney viscosity within the range between 35 and 60, and material having an average molecular weight above about 55000, regardless of the molecular weight range, has a Williams plasticity above 145 and a Mooney viscosity above 60.

In the past the value of the molecular weight and therefore the Williams plasticity and Mooney viscosity have been found to be a function of the lowness of the temperature at which the polymerization is conducted; a function of the purity of the raw materials and a function of the potency of the catalyst, but great difficulty

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has been encountered in controlling these factors sufficiently well to obtain consistently a polymer having the desired plasticity and the desired molecular weight range, and of a sufficiently narrow molecular weight range to be satisfactorily processable and curable to a good tensile strength. That is, the molecular weight may be decreased and plasticity increased by polymerization at a higher temperature, but an increase in temperature is undesirable since it makes the polymerization process difficult to operate because of the increased stickiness of the slurry of polymer in reaction liquid. Likewise, it is desirable that materials of the highest purity be used, since the uncontrolled presence of unknown impurities causes a wholly unpredictable and uncontrollable reduction in molecular weight. Also, the most potent possible catalyst is desirable, since catalysts of lower potency yield materials which are undesirable in many ways.

The present invention is based upon the discovery that it is possible to control the plasticity by control of the molecular weight, the range of molecular weight being controlled by the steps of purifying the olefins to a high degree of purity, operating at a comparatively very low temperature with a highly potent catalyst, and controlling the reaction by the presence of modifying agents in the reaction mixture which have the effect of limiting the maximum molecular weight obtainable and narrowing the range of molecular weight to bring the plasticity to the desired range of values.

For this purpose it is desirable that very low temperatures, such as from  $-70^{\circ}$  to  $-103^{\circ}\text{C.}$ , be used with olefinic material of high purity, preferably isobutylene having a purity of from 96 to 98% by weight or better and diolefins having a purity from 86 to 99% or better. There are then added to the mixture small amounts, ranging from 0.001% to 15% of the modifying material. The modifying material is conveniently a substituted hydrocarbon having a non-metallic substituent selected from Groups 5 and 6 of the Periodic Table; such substances as the various alcohols, aldehydes, ethers, or organic acids being particularly suitable, along with the organic sulfides such as the mercaptans and their analogs and homologs, and the various nitrogen substituted compounds, especially the amines, as well as their analogs and homologs. (The organic phosphorus, arsenic, antimony and bismuth compounds operate similarly, but the tendency toward instability and cost of such compounds makes them less desirable for this invention). Olefins of

higher molecular weight than the reactants such as diisobutylene, octene, or triisobutylene, are common compounds which are particularly effective. The normal  $\text{C}_4$  and higher olefins such as normal butylene, normal amylenes, are also very effective, and even the isoolefins, higher than isobutylene, are effective modifiers when added to the isobutylene containing reactant mixture. The reaction is then conducted by the application of a solid or liquid Friedel-Crafts catalyst in solution in a low-freezing, inert solvent. A preferred catalyst solution consists of aluminum chloride in solution in a low-freezing solvent such as ethyl or methyl chloride or carbon disulfide. The resulting polymerization then yields a polymer having an advantageous plasticity and molecular weight which is readily cured to a material of high tensile strength, and, in addition, is readily milled, extruded and otherwise processed.

Thus an object of the invention is to modify the course of an olefinic polymerization reaction by the presence of bodies which alter the course of the reaction to control the plasticity by limiting the maximum molecular weight obtained to a value below about 60000; and to narrow the range of molecular weight material obtained.

It has been proposed in the past to add materials such as vulcanization aids and fillers to the reaction mixture before polymerization.

It has been proposed in Patent Specification No. 525,542 to employ in the low temperature polymerization of isobutylene or its mixtures with a minor proportion of diolefins using boron fluoride as a catalyst, an accelerator consisting of sulfuric, nitric, caproic, or chloracetic acid, formaldehyde phenol, cresol, or monohydric aliphatic, cycloaliphatic or aromatic alcohols. Such organic materials act as poisons rather than accelerators when used with the catalyst solutions employed in the present invention.

Furthermore, in my foreign correspondents earlier Patent Specification No. 560,924, it is disclosed that when isoolefins and non-conjugated diolefins such as dimethallyl are copolymerized at low temperatures to give a solid copolymer insoluble in most organic solvents, then the addition of poisons such as diisobutylene and the normal olefins gives rise to an oily liquid copolymer in place of the solid polymer.

It has also been proposed, in my foreign correspondents earlier Patent Specification No. 577,350, to add metal soaps to olefinic polymerization feed-stocks employed in low temperature polymeriza-

tion using a Friedel-Crafts catalyst, whereby the polymers formed are obtained in a finely-divided non-adhesive condition.

The present invention is directed to a means of producing solid rubbery polymers, in which the maximum molecular weight of the solid polymer is controlled by the addition of controlled amounts of organic polymerization poisons to the reaction mixture.

Thus the present invention comprises a polymerization process for the polymerization of mixtures of a major proportion of a pure isoolefin with minor proportions of a pure diolefin or of a pure polyolefin at temperatures ranging from  $-40$  to  $-165^{\circ}\text{C.}$ , to form a solid copolymer, by the application thereto of a solution of a solid or liquid Friedel-Crafts catalyst in a low-freezing inert solvent, wherein the maximum molecular weight of the solid copolymer is limited by the addition to the reaction mixture of from  $0.001\%$  to  $15\%$  by weight of an organic modifying agent selected from one or more of the following classes, viz. substituted hydrocarbons having a non-metallic substituent selected from Groups V and VI of the Periodic Table, with or without halogen,  $\text{C}_4$  and higher normal olefins,  $\text{C}_5$  and higher isoolefins and aromatic hydrocarbons.

In practising the invention, the polymerization mixture may be prepared from an isoolefin which is preferably isobutylene, but may be other isoolefins such as 2-methyl butene-1 or 2-methyl pentene-1, or the like. This material is used in major proportion with a minor proportion of a polyolefin such as butadiene or isoprene or piperylene or dimethyl butadiene or the tri-olefin, myrcene, or dimethallyl, the preferred polyolefins having from 4 to 14 carbon atoms per molecule. The olefinic material is cooled to a temperature below  $-40^{\circ}\text{C.}$ ; preferably within the range of  $-70^{\circ}\text{C.}$  to  $-103^{\circ}\text{C.}$ , although the temperature may be brought as low as  $-127^{\circ}\text{C.}$  or even as low as  $-164^{\circ}\text{C.}$  by the use of suitable refrigerants. The low temperatures may be obtained by the addition of the appropriate refrigerant such as solid carbon dioxide or liquid methane or liquid ethylene or liquid ethane or even liquid propane directly to the reaction mixture; or the material may be cooled by a refrigerating jacket containing similar refrigerants applied to the reaction vessel. When the desired low temperature is obtained, the polymerization is conducted by the application to the olefinic mixture of an appropriate polymerization catalyst.

The catalyst consists of a Friedel-Crafts type catalyst as shown by N. O. Calloway in his article on "The Friedel-Crafts

Synthesis" printed in the issue of "Chemical Reviews" published for the American Chemical Society at Baltimore in 1935 in Volume XVII No. 3, the article beginning on page 327, the list being particularly well shown in Table 2 on page 375. Of these catalysts the aluminum halides are preferred, but titanium and uranium halides are also excellent catalysts, the other suggested Friedel-Crafts catalysts being of varying power and efficiency. These catalysts may also be modified in various ways to yield double salts or hydrates or the like which are also of high catalytic potency.

The Friedel-Crafts catalyst is dissolved in a suitable solvent such as ethyl or methyl chloride or carbon disulfide which are the preferred solvents. Alternatively, any of the mono or poly alkyl halides having carbon atom numbers up to 5 are useful, depending upon the freezing point which necessarily is below  $0^{\circ}\text{C.}$ , (the low freezing, as above pointed out, means having a freezing point substantially below  $0^{\circ}\text{C.}$ , preferably a substantial number of degrees below). It is necessary also that the solvent should not form a complex with the Friedel-Crafts substance, but should distill away from the catalyst substance at approximately the boiling point of the solvent, leaving substantially none of the solvent attached to or combined with the Friedel-Crafts substance.

During the preparation of the polymerization mixture, the modifying agent is added to the olefinic material in amounts ranging from  $0.001\%$  on the amount of olefin to  $15\%$ . An excellent reaction modifier is isobutylene dimer or trimer or other substance as hereinafter pointed out. In the preparation of the polymerization mixture, it is desirable, although not necessary, that the mixture be diluted with an appropriate diluent or diluent refrigerant. When the mixture is cooled by admixed liquid ethylene, it serves simultaneously as diluent and refrigerant. Alternatively, and especially when a refrigerating jacket is used, the material may, if desired, be diluted with such substances as methyl or ethyl chloride, carbon disulfide, *n*-butane, and other saturated hydrocarbons which are liquid at the reaction temperature. When the reaction mixture is complete with the modifier present, the reaction is conducted by adding the catalyst to the cold olefinic material preferably in the form of fine droplets onto the surface of the rapidly stirred olefinic material. Alternatively, the catalyst solution may be delivered to the reaction mixture in any convenient way which provides a rapid dispersal of the catalyst solution into the body of the

reaction mixture. It may be delivered through a jet into the bottom of the rapidly stirred reaction mixture; or the materials may be combined together in a high turbulence zone such as the eddy zone adjacent a propeller stirrer, or into a rapidly flowing stream of material.

The reaction proceeds rapidly to yield the desired polymer having a plasticity and molecular weight which is readily adjusted, by the amount of modifier present to have a Williams plasticity between 100 and 145, a Mooney viscosity between 35 and 60; and an average molecular weight between 30000 and 65000, the best results usually being obtained with molecular weights of 35000 to 55000.

The modifier may, as above pointed out, consist of isobutylene dimer or trimer or may be olefins such as the normal amylene, or the hexenes or the heptenes or the octenes (diisobutylene may be regarded as an isooctene) or the nonenes or decenes or even higher substances of this type.

In addition, the alcohols having from one up to 18 or 20 or higher carbon atoms per molecule including methyl, ethyl, propyl, allyl, tert.-butyl, octyl and stearyl alcohols and also benzyl alcohol and its analogues. The ketones including acetone, acetophenone, methyl ethyl ketone, methyl stearyl ketone, are also advantageous. Likewise, the organic acids such as acetic, butyric, *o*-toluic, oleic, stearic and the like are excellent modifiers as are also their esters. The thioacids including thioacetic dithiopropanic and thiobenzoic acids are also very effective. The esters including ethyl acetate, methyl oleate, methyl furoate, phenyl valerate, stearin, ethyl thioacetate, are also efficient modifiers. The amides including such substances as di-*N*-methylacetamide, di-*N*-ethylbenzamide, substituted stearamides and propionamide likewise are effective modifiers. The nitriles including such substances as methyl cyanide, metatolyl cyanide and acrylonitrile likewise are excellent modifiers. The organic sulfides and mercaptans including methyl mercaptan, dimercaptoethane, propyl mercaptan, dodecyl mercaptan also are advantageous modifiers. Likewise the ethers including methyl ether, ethyl ether, ethyl phenyl ether, dioxane, furane, are also effective modifiers. The sulfides, including diethyl sulfide, dimethyl sulfide, ditolyl sulfide, bis-tert.-amylphenol sulfide are also excellent modifiers.

The polysulfides including dimethyl disulfide, diethyl disulfide, ditolyl disulfide, diamyl tetrasulfide are also very effective. The sulfoxides including dimethyl sulfoxide, diethyl sulfoxide, ethyl phenyl

sulfoxide are also advantageous. The sulfones including dimethyl sulfone, dipropyl sulfone, di-*o*-tolyl sulfone are also efficient modifiers. The sulfonates including ethyl benzene sulfonate, methyl ethyl sulfonate, isopropyl hexyl sulfonate are also very effective. The sulfates including methyl sulfate, ethyl sulfate, diethyl sulfate also are advantageous modifiers. The acid halides including acetyl chloride, *p*-ethylbenzoyl chloride, propionyl bromide, stearyl chloride, are also efficient modifiers. The anhydrides including acetic anhydride, toluic anhydride likewise are excellent modifiers. The amines including propylamine, ethanolamine, dimethyl aniline, pyridine, pyrrole are also very effective. The nitro compounds including nitropropane, nitrobenzene, nitroethane, tetranitromethane also are advantageous modifiers. The nitroso compounds including nitrosotoluene, nitrosophenol, nitrosodimethyl aniline likewise are effective modifiers. The nitrates including ethyl nitrate, butyl nitrate, isopropyl nitrate also are advantageous modifiers. The nitrites including isoamyl nitrite, butyl nitrite, and ethyl nitrite are also very effective. The hydroxylamines including *o*-ethylphenyl hydroxylamines, tolyl hydroxylamine and ethyl hydroxylamine are also advantageous. The selenides including diethyl selenide, phenyl ethyl selenide, methyl propyl selenide are also excellent modifiers.

It will be noted that these compounds contain oxygen or nitrogen or sulfur, or selenium, or are acidic bodies. They are all defined and identified as substances which react with aluminum chloride to give complexes.

Other advantageous modifiers include such substances as the substituted alcohols of the type of ethylene chlorohydrin, ethylene cyanohydrine, nitro ethyl alcohol, 2-amino ethyl alcohol,  $\beta$ -ethoxy ethyl alcohol; likewise, the substituted acids including such substances as chloroacetic acid,  $\beta$ -bromopropionic acid, ortho-nitrobenzoic acid, alpha-hydroxycaprylic acid and ortho-chloro-para-nitrobenzoic acid. Likewise, the substituted phenols including such substances as meta-chlorophenol, ortho-nitrophenol and tertiary-butyl catechol are particularly useful. Other valuable modifiers include such substances as dicvandiamides, such as di-*n*-butyl dicvandiamide; metallic alcoholates, such as titanium ethylate; sulfonamides, such as *N*-di-*n*-butyl benzene sulfonamide; phenols, such as *p*-tertiary amylphenol; ureas, such as sym. di-*n*-butylurea; cyclic dinitrogen compounds such as pyrimidine and pyrazoline; and acetylene.

Thus, it will be noted that a portion of the list of useful modifiers includes substantially all of the substituted hydrocarbons which contain non-metallic substituents from Groups 5 and 6 of the Periodic Table, including particularly all of the oxygen compounds, all of the sulfur-containing compounds (which contain hydrogen as well), all of the selenium compounds, all of the tellurium compounds (polonium substituted compounds obviously are similarly effective but they are commercially unfeasible because of the extremely small amount of polonium available and its inordinately high price). Likewise the modifiers include the nitrogen substituted hydrocarbons and the phosphorus and arsenic, substituted compounds insofar as they are sufficiently stable to be useful.

In addition, substantially all of the normal monoolefins up to 35 carbon atoms per molecule are useful, the principal requirement being that they be either mixable with, or soluble in, the reaction mixture in amounts greater than 0.001%. It is also found that some of the less easily polymerizable polyolefins are also effective as modifiers, particularly those having carbon numbers per molecule above 14. It is found that when there are two polyolefins present with the preferred isobutylene in the reaction mixture, one of which is an easily copolymerizable material such as butadiene or isoprene or piperylene or dimethyl butadiene or myrcene or dimethylallyl, and the other a less easily polymerizable polyolefin such as chloroprene, the less easily polymerizable polyolefin serves as a modifier just as do the substituted hydrocarbons or normal olefins above mentioned.

Also the aromatic hydrocarbons are effective and efficient modifiers. Benzene and its homologs including in addition toluene, xylene, cumene, and also the polyaromatics including naphthalene, are effective modifiers but must be present in somewhat larger quantities than is the case with some of the other modifiers.

When the reaction has reached the desired stage, it may be halted by dumping the reaction mixture into warm naphtha containing small amounts of alcohol or into warm water or warm soda solution or warm dilute aqueous alcohol or the like to drive off volatile materials and inactivate the catalyst; or the reaction may be allowed to complete itself before recovering the polymer. The solid polymer may then be milled, and if desired, washed on the mill to remove as much as possible of the last traces of the catalyst and free the material entirely from dissolved volatile substances. The material

may then be compounded with pigments, sulfur and sulfurization aids or other curing agents and cured at appropriate temperatures for appropriate times to yield the desired structural element.

In the following examples all parts are by weight unless otherwise stated.

#### EXAMPLE I.

A mixture was prepared consisting of 1480 parts of isobutylene of 96% purity, 21 parts of isoprene of 93% purity, and 2700 parts of methyl chloride of 99% to 99.7% purity all parts being by weight. The mixture was placed in a storage container having a refrigerating jacket, filled with liquid ethylene. The refrigerant brought the temperature of the mixture down to  $-90^{\circ}$  to  $-110^{\circ}\text{C}$ . A portion, approximately  $1/3$  of the mixture, was transferred to a refrigerant jacketed reactor and polymerized without modification by application to the rapidly stirred solution of olefinic material in methyl chloride of 120 parts by weight per 1000 parts of polymerization mixture, of a solution of aluminum chloride in methyl chloride having a concentration of 0.2%; the catalyst solution being applied in the form of a fine spray onto the surface of the separately stirred polymerization material.

A second portion of 1400 parts was taken and 0.7 parts of diisobutylene per 1400 of reaction mixture were added to the solution of olefinic material in methyl chloride and well stirred in. 200 parts of the same catalyst solution were similarly applied to the second portion for a second polymerization.

To the third portion there was then added 1.05 parts of diisobutylene instead of the 0.7 parts as with batch 2, and portion 3 was then polymerized in the same manner as portions 1 and 2.

All three portions were polymerized to approximately 60% yield and then dumped into warm water. Each portion of solid polymer was then removed from the warm water and the batches were separately washed and dried on the mill. The three portions were then separately compounded according to the following recipe:

Polymer	-	-	100 parts	
Carbon Black	-	-	10 "	120
Stearic Acid	-	-	3 "	
Zinc Oxide	-	-	5 "	
Sulfur	-	-	1.5 "	
Tetra methyl thiuram disulfide	-	-	1 "	125

A part of each portion was cured at a temperature of  $307^{\circ}\text{F}$ . for a time interval of 60 minutes while another portion of each batch of uncompounded polymer was

used for the determination of plasticity according to the Williams System. Test samples were cut from the cured portions for the determination of tensile strength,

and molecular weight was determined on uncompounded samples by the Staudinger Viscosity Method. The inspection results are shown in the following Table I:

TABLE I

Portion No.	Molecular Wt.	Williams Plasticity	Plasticity Recovery	Tensile Strength
1	74000	202	38	3730
2	45000	138	16	3410
3	35500	114	6	3170

These inspection results show the very great gain in plasticity obtainable by the reduction in molecular weight, and show the minor loss only of tensile strength.

Other determinations on similar samples

show that portion 1 with the 74000 molecular weight extrudes with great difficulty and the extruded material is rough, off size, and generally unsatisfactory. In contrast, the 45000 molecular weight

shows reasonably good extrusion properties, the extruded sample being smooth to fair and of reasonably accurate size. The third portion of 35500 molecular weight shows very good extrudability, a close

size, a very smooth finish, and a high rate of extrudability. Thus, the third portion is highly desirable for extruded tubing; tire inner tubes; and extruded tread stock as well as calendered goods

generally.

#### EXAMPLE 2

A mixture was prepared consisting of 800 parts by volume of isobutylene, 200 parts of butadiene, and 2000 parts of liquid ethylene. This material was divided into four portions. The first portion was polymerized at  $-100^{\circ}\text{C}$ . by the application to the cold mixture of approximately 70 parts by volume of a 0.6% solution of aluminum chloride in methyl chloride. The second portion was modified by the addition thereto of 0.05% (0.125 parts to 250 parts of olefinic material) of ethyl ether, based on the isobutylene and butadiene. Portion 3 was modified by the addition of 0.1% of ethyl ether (0.25 parts per 250 parts). Portion 4 was modified by the addition of 0.2% of ethyl ether on the isobutylene-butadiene content (0.5 parts per 250 parts). All four portions were similarly polymerized to a yield of 50 to 60% of the isobutylene-butadiene present and when this stage of polymerisation was reached, the cold mixtures were dumped into warm water to inactivate the catalyst and to volatilize out the unpolymerised material. The respective portions of solid polymer were then washed and dried on the mill and samples taken on which the molecular weight was determined by the Staudinger method. The respective portions were then separately compounded

on the mill according to the recipe in Example I: samples of the raw compound were tested for Williams plasticity; other samples were cured as in Example I and the tensile strength determined.

The Williams plasticity and tensile strength were found to be similar to those in Example I and the molecular weights, as determined, are shown in the following Table II.

TABLE II

Portion No.	Mooney Viscosity	Molecular Weight
1 (no modifier)	80	71000
2	61	58000
3	50	47000
4	44	43000

These samples show the same range of properties as was obtained in Example I, and show the improvement in the physical properties obtainable by the process of the present invention.

#### EXAMPLE 3

A mixture was prepared consisting of 160 parts by weight of isobutylene of 96% purity, 5 parts by weight of isoprene of 93% purity, and 1000 parts by weight of methyl chloride of 99 to 99.7% purity. This mixture was cooled, as in Example I, to a temperature of  $-100^{\circ}\text{C}$ . and successive portions were polymerized at that temperature by the addition of 100 parts by weight of a solution of aluminum chloride in methyl chloride having a concentration of 0.2%, as in Example 1. The mixture was divided up into four portions, and as each portion was prepared for polymerization, it was treated with butene-2, as shown in Table III; the first portion containing no butene-2, the second portion containing 2.5%, the 3rd portion 5%, and the 4th portion 7.5% based on the olefins present. These successive portions were then polymerized, as in Example I, and the Williams plasticity determined on the uncured materials to yield the values shown in Table III below. The respective polymers were then compounded according to the recipe in Example I, cured, as in Example I, and the tensile strength determined to yield the results shown in Table III. These results clearly show the effectiveness of the present treatment in

bringing the Williams plasticity value within the desired range, without sacri-

fice of tensile strength or other valuable properties.

5

TABLE III

Portions	Volume % Butene-2	Tensile Strength	Molecular Weight	Williams Plasticity	Recovery
1	None	3600	66000	180	36
2	2.5	3390	57000	155	24
3	5	3285	43000	110	14
4	7.5	3200	37000	108	5

Thus, these results further show the utility of the present invention.

## EXAMPLE 4

15 A similar mixture to that in Example 3 was prepared, divided into five portions, and successive portions treated with 0%, 1%, 2.5%, 5% and 10% of butene-1. The several portions were then separated, poly-

merized, as in Examples 1 and 3 and the 20 molecular weights of the polymers and Williams Plasticity values determined, as shown in Table IV. The polymers were then separately compounded according to the recipe of Example 1, cured for 40 25 minutes and 60 minutes at 153°C. to yield the tensile strengths shown in Table IV.

TABLE IV

TABLE IV					
30	Volume %	Staudinger	Tensile Strengths		Mooney
	Butene-1	Molecular Weight	40' Cure	60' Cure	Viscosity
	None	87000	3700	3550	82
	1.0	77000	3850	3650	80
	2.5	70000	2850	2850	68
	5.0	53000	3250	3500	51
	10.0	49000	3450	3150	45

35 These results further show the efficacy of the procedure of the present invention.

## EXAMPLE 5

A mixture was prepared consisting of 1200 parts by volume of methyl chloride, 99 to 99.7%, 300 parts by volume of isobutylene of 96% purity, and 5.4 parts by volume of isoprene of 93% purity. This mixture was cooled by a refrigerating jacket on the container having liquid ethylene therein, bringing the tempera- 45 ture to -100°C. 3 separate portions of this mixture were separately polymerized by the addition of 100 parts by volume per 1500 parts of reaction mixture of a solu- 50 tion of aluminum chloride in methyl chloride having a concentration of 0.3%.

The catalyst was applied in the form of a fine spray onto the surface of the rapidly stirred reaction mixture. The first portion contained no modifier. The second 55 portion contained 2.5 parts by volume of trimethyl ethylene per 100 parts by volume of isobutylene in the reaction mixture, and the third portion contained 5 parts by volume of trimethyl ethylene per 100 parts of isobutylene in the mixture. 60 The several polymerization mixtures after polymerization to 70% yield were dumped into warm water to flash off the methyl chloride and unreacted olefins. Molecular 85 weights and Williams plasticity values for the respective portions of polymer were determined, as shown in Table V.

TABLE V

Run No.	Volume % Trimethylethylene based on Isobutylene	Staudinger Molecular Weight	Williams Plasticity
1	None	56000	160
2	2.5	34000	108
3	5.0	25000	95

75

## EXAMPLE 6

A mixture was prepared consisting of 985 parts by volume of isobutylene of 96% purity with 15 parts by volume of piperylene and 2000 parts by volume of liquid ethylene. This mixture was divided into 3 portions which were separately polymerized after the addition of 0.04 parts per 100 parts of reactants, and 0.05 parts of ethyl ether per 100 parts of reactants. The 85 catalyst consisting of a 0.5% solution of

aluminum chloride in methyl chloride applied to the surface of the rapidly stirred reaction mixture as in the previous examples. Williams plasticity values and molecular weight values were deter- 90 mined on the raw polymer. The polymer was then compounded according to the recipe of Example 1, and tensile strengths determined to yield the results shown in Table VI. 95

TABLE VI

	Volume % Ethyl Ether based on the Reactants	Staudinger Mol. Wt.	Maximum Tensile Strength	Mooney Viscosity
5	None	68000	3200	77
	0.04	55000	3000	38
	0.05	49000	3300	47

These results further show the value and utility of the present invention.

## EXAMPLE 7

- 10 A mixture was prepared consisting of 215 parts by weight of isobutylene of 96% purity and 3.12 parts by weight of isoprene of 93% purity together with 1050 parts by weight of methyl chloride of 99 to 99.7% purity. This material was divided into two portions and polymerized by the application thereto of 88 parts by weight per 215 parts by weight of isobutylene of a catalyst consisting of a 0.20% solution of aluminum chloride in methyl chloride;

the first portion being polymerized alone, the second portion being polymerized after the addition of 0.15 parts per 100 parts of isobutylene of methyl alcohol. 25

The two polymerizations were then separately dumped into warm water and the molecular weight and Mooney plasticity determined on the raw polymer. The respective batches of polymer were then compounded according to the recipe in Example 1, cured at 307°F. for 60 minutes and the tensile strength determined. The results are shown in the following Table VII:— 35

TABLE VII

	Run No.	Addition of Methyl Alcohol	Staudinger Mol. Wt.	Mooney Viscosity	Tensile Strength of 50 parts channel black cure (60' at 307°F.)
40	1	None	74000	74	3000
	2	0.15%	47000	45	3000

These results likewise show the improvements in plasticity of the materials without sacrifice of tensile strength.

## EXAMPLE 8

- 45 A mixture consisting of 1200 parts by volume of methyl chloride, 300 parts by volume of isobutylene of 96% purity, and 5.4 parts by volume of isoprene was cooled, as in Example 5, divided into 3 parts, and polymerized by a catalyst, as in Example 5; 1 part being polymerized without modifier; the second part being

polymerized after the addition of 0.002 parts by volume of acetone per 100 parts 55 of mixed methyl chloride, isobutylene and isoprene; the third portion being polymerized after the addition of 0.005 parts of acetone per 100 parts of reaction mixture. The resulting polymer mixtures 60 were dumped into warm water, as in Example 5, and the Mooney viscosity of the respective samples of raw polymer were determined along with the molecular weights, as shown in Table VIII. 65

TABLE VIII

	Experiment No.	Wt. % of Acetone Based on Total Feed	Staudinger Mol. Wt.	Mooney Viscosity
70	1	None	52000	71
	2	0.002	41000	67
	3	0.005	35000	53

- 75 These samples were then compounded according to the recipe in Example 1 and the tensile strengths and elongations were found to be excellent, although precise determinations were not made.

## EXAMPLE 9

- 80 A similar polymerization mixture was prepared, as in Examples 5 and 8; divided into 5 portions and polymerized; one

without the presence of modifiers, and the other 4 after the addition of varying amounts of acetaldehyde, including 0.002 parts by weight, 0.005 parts by weight, 0.01 parts by weight, 0.02 parts by weight 85 of acetaldehyde per 100 parts by weight of polymerization mixture.

The polymer was purified and evaluated as in Examples 5 and 8 to yield the results shown in Table IX:— 90



TABLE IX

Run No.	Weight % of Acetaldehyde based on the Total Feed	Staudinger Mol. Wt.	Mooney Viscosity
1	None	50000	76
2	0.002	40000	58
3	0.005	39000	53
4	0.01	36000	43
5	0.02	28000	33

These results show the efficacy of  
10 acetaldehyde as a modifier.

## EXAMPLE 10

A similar mixture of polymerization  
material was prepared as in Examples 5  
and 8; divided into 6 portions and after

treatment with various modifiers as shown 15  
in Table X, it was polymerized as before.  
The molecular weights and Mooney vis-  
cosities were determined as shown in  
Table X. The results obtainable by these  
various substances are well shown in the 20  
following Table X:—

TABLE X  
Wt. % of Ester  
Based on Total  
Feed

Run No.	Ester	Staudinger Mol. Wt.	Mooney Viscosity
1	None	56000	76
2	Methyl Oleate	40000	46
3	"	36000	40
4	Isoamyl Butyrate	25000	33
5	None	46000	72
6	Amyl Stearate	43000	52

These results show the effectiveness of a  
number of esters in controlling the plas-  
ticity of the finished polymer.

## EXAMPLE 11

A mixture was prepared consisting of  
800 parts by volume of isobutylene of 96%  
purity and 200 cc's of butadiene of 95%  
purity together with 2000 parts by volume  
40 of liquid ethylene. This material was

divided into 3 portions as before and poly-  
merized by the addition of 100 parts by  
volume per 1000 parts of reaction mixture  
of an 0.5% solution of aluminum chloride  
in methyl chloride. To two of the por-  
tions, varying amounts of dodecyl mer-  
captan were added. The polymerization  
was conducted as before and similar  
inspection determinations were made; the  
resulting values are shown in Table XI. 50

TABLE XI

Run No.	% Dodecyl Mercaptan Based on Reactants	% Conversion	Staudinger Mol. Wt.	Mooney Viscosity
1	None	43	88000	82
2	0.05	38	78000	81
3	0.25	42	41000	49

These results show the value of the  
mercaptans as modifiers.

## EXAMPLE 12

A similar mixture to that in Example  
8 was prepared and similarly treated,

after being divided into 5 portions, to  
which various amine modifiers were added,  
as shown in Table XII to yield polymers  
having the properties shown. 65

TABLE XII  
Wt. % of Amine  
Based on Total  
Reactants

Run No.	Type of Amine	Staudinger Mol. Wt.	Mooney Viscosity
1	Tributylamine	38000	45
2	None	48000	59
3	Lorolamine	40000	41
4	"	33000	28
5	Trimethylamine	30000	35

These results show the efficacy of the  
amines as reaction modifiers.

## EXAMPLE 13

A similar polymerization mixture was

prepared to that in Example 8 and por-  
tions were treated with oleic acid and  
sulfur dioxide. Upon polymerization and  
evaluation, inspection results were  
obtained, as shown in Table XIII.

TABLE XIII  
% Additive  
Based on the  
Total Feed

Run No.	Additive	Staudinger Mol. Wt.	Mooney Viscosity
5	1 None	56000	78
	2 Oleic Acid	33000	32
	3 None	49000	77
	4 Sulfur Dioxide	37000	59

These results show the efficacy of  
10 acidic bodies generally as reaction  
modifiers

#### EXAMPLE 14

Two reaction mixtures were prepared  
consisting each of 1050 parts by volume  
15 of methyl chloride, 450 parts by volume  
of isobutylene of 99% purity and 6.75  
parts by volume of isoprene of 96% purity.  
These mixtures were cooled to  $-100^{\circ}\text{C}$ .  
by application of a refrigerating jacket to  
20 the reaction vessel and polymerization was  
conducted by the addition to the cold

mixture of a solution of aluminum  
chloride in methyl chloride of 0.5% con-  
centration, as in the previous examples for  
one mixture. The second mixture was 25  
prepared with the further addition thereto  
of 100 parts by volume of benzene (benzol)  
before the polymerization step.

The resulting solid polymers were  
evaluated for Williams plasticity and were 30  
then compounded according to the recipe  
given in Example 1, and the tensile  
strength after 40-minute and 60-minute  
cures determined. These results are pre-  
sented in the following Table XIV:— 35

TABLE XIV

Run No.	Description	Williams Plasticity	Tensile Strength 40' Cure	60' Cure
	1 Run containing no benzene	163—27	3900	3800
40	2 Run containing 100 cc. benzene	140—14	3750	3700

These evaluations show the effectiveness  
of the benzene in improving the plasticity  
without adversely affecting the tensile  
strength of the product.

45 These results show clearly the effec-  
tiveness of the modifiers and the utility of  
the results obtained thereby in the way of  
plasticity, ease of extrusion, ease of calen-  
dering and good tensile strength. The  
50 Tables do not show determinations of the  
values or other physical properties but  
these polymers likewise show very high  
abrasion resistance, very high flexure  
resistance and advantageously low heat  
55 build-up as well as a high resistance to  
oxygen and breakdown from ozone and  
other influences.

Thus the process of the invention  
merely improves the calendering, extrud-  
60 ing and processing properties of a rubber-  
like olefinic polymer while retaining the  
advantageous tensile strength and other  
valuable properties of the polymer as well  
as its ready curability.

65 In Specification No. 589,393 also a com-  
munication from my foreign correspon-  
dents and which bears the same date as  
the present Application, there is described  
and claimed a process for copolymerizing  
70 isobutylene and a  $\text{C}_4$ — $\text{C}_{14}$  polyolefin  
together with 0.001% to 1% of an ether,  
the mixture being polymerized in the  
presence of a Friedel-Crafts catalyst at a  
temperature from  $-20^{\circ}\text{C}$ . to  $-165^{\circ}\text{C}$ .  
75 under the influence of the pulling action

of kneader blades. In the present Appli-  
cation, I make no claim to the process  
claimed in Specification No. 589,393.

Having now particularly described and  
ascertained the nature of the said inven- 80  
tion and in what manner the same is to  
be performed, as communicated to me by  
my foreign correspondents, I declare that  
subject to the above disclaimer what I  
claim is:— 85

1. A process for the polymerization of  
mixtures of a major proportion of a pure  
isolefin with minor proportions of a pure  
diolefin or of a pure polyolefin at tem-  
peratures ranging from  $-40$  to  $-165^{\circ}\text{C}$ . 90  
to form a solid copolymer by the applica-  
tion thereto of a solution of a solid or  
liquid Friedel-Crafts catalyst in a low-  
freezing inert solvent, wherein the maxi-  
mum molecular weight of the solid copoly- 95  
mer is limited by the addition to the reac-  
tion mixture of from 0.001% to 15% by  
weight of an organic modifying agent  
selected from one or more of the following  
classes, viz. hydrocarbons having a non- 100  
metallic substituent selected from Groups  
V and VI of the Periodic Table, with or  
without halogen,  $\text{C}_4$  and higher normal  
olefins,  $\text{C}_5$  and higher isoolefins and  
aromatic hydrocarbons. 105

2. A process according to Claim 1,  
wherein the said modifying agent is an  
alcohol having from 1 to 18 carbon atoms  
per molecule, a ketone, an ether, an ester,  
an organic acid, a mercaptan, an amine, 110

a thio organic acid, an amide, a nitrile, an alkyl, aryl or aralkyl sulfide or polysulfide, sulfonate, or sulfate, an organic acid halide or anhydride, a nitro hydrocarbon, a nitroso hydrocarbon or substituted hydrocarbon, an alkyl, aryl or aralkyl nitrate or nitrite, a hydroxylamine, an alkyl, aryl or aralkyl selenide, a substituted alcohol, a substituted organic acid, or a substituted phenol.

3. A process according to Claim 1, wherein the said modifying agent is a normal olefin having from 4 to 35 carbon atoms per molecule.

4. A process according to Claim 1, wherein the modifying agent is diisobutylene, ethyl ether or butene-2.

5. A process according to any of the preceding Claims, wherein the isoolefin is isobutylene.

6. A process according to any of the preceding Claims, wherein the diolefin has from 4 to 14 carbon atoms per mole-

cule, and is preferably butadiene, isoprene or dimethyl butadiene.

7. A process according to any of the preceding Claims, wherein the olefins to be polymerized comprises a mixture of isobutylene with a minor proportion of isoprene, the reaction temperature is between -90 and -110°C. and the catalyst is a solution of aluminum chloride in methyl chloride.

8. A process according to Claim 7, wherein the modifying agent is methyl alcohol or a second mono-olefin.

9. A process according to any of Claims 1 to 6, wherein the said organic modifying agent is an aromatic hydrocarbon such as benzene, toluene, xylene or cumene or naphthalene.

Dated this 14th day of November, 1944.

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